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63-2-4

Office of Naval Research

Contract No. N62558 - - - 2381

Task No. NR051 - - - 417

Technical Report No. 4

Reduction by Organometallic Complexes.

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ASTIA
DEC 25 1963

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In a recent paper (1), Wilkinson and co-workers discussed the protonation of transition metal carbonyl complexes; solutions of tricarbonylarenechromiums in concentrated acids were found to decompose rapidly but N.M.R. evidence for protonation at the metal atom was obtained under these conditions. Sternberg and Wender (2) have explained previously the reducing ability of the dicarbonyl- π -cyclopentadienyliron dimer in ethanolic hydrochloric acid in terms of protonation at the iron atom but no direct spectral evidence is available to support this contention (1). Publication of these results prompts us to record some preliminary observations of the behaviour of tricarbonylarene chromiums in dilute ethanolic hydrochloric acid which are consistent with the above view. We find that solutions of azobenzene (10^{-2} M) and tricarbonylarenechromiums (10^{-2} M), $\text{RC}_6\text{H}_5(\text{CO})_3$, in dilute ethanolic hydrochloric acid (10^{-1} M) under nitrogen give fair yields (up to 30%) of benzidine dihydrochloride, identified by analysis and I.R. spectrum. The reaction occurs for the substituent range $\text{R}=\text{Me}, \text{Cl}, \text{H}, \text{NH}_2, \text{NHMe}$ and NMe_2 and is facilitated by electron repelling groups; this is consistent with protonation at the chromium atom being assisted by charge transfer as discussed by two of us previously (3). Moreover, no reduction is observed in the absence of acid so some type of protonation seems essential. More dilute solutions (10^{-4} M) of the complexes undergo fairly rapid decomposition (complete in 30 mins.-2 hours) in ethanolic hydrochloric acid under nitrogen with the evolution of carbon monoxide and formation of free arene. Spectrophotometric studies of tricarbonylanilinechromium show an immediate fall in intensity of the 3150 \AA band corresponding to

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protonation at the nitrogen atom followed by a further decrease due to decomposition; extrapolation gives a pKa value of 1.26. In contrast, a rapid potentiometric titration, under nitrogen, gives a pKa of 2.15. The difference may be ascribed to additional protonation at the metal atom.

In the presence of an oxidant, reduction apparently occurs by proton transfer from the protonated complex with, consequently, less direct decomposition. Increase of reaction temperature favours the latter and the yields of benzidine are correspondingly lower. These results support the view that reduction by organo-metallic complexes is related to protonation at the metal atom. Detailed investigations of these reactions are in progress.

- (1) Davison, McFarlane, Pratt and Wilkinson, J., 1962, 3653.
- (2) Sternberg and Wender, Internat. Conf. Coordination Chemistry, Chem. Soc. Special Publ. No. 13, 1959, p. 35.
- (3) Brown and Sloan, J., 1962, 3846.

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